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ON THE STRUCTURE OF PHOSPHORUS COMPOUNDS

R. Wolf

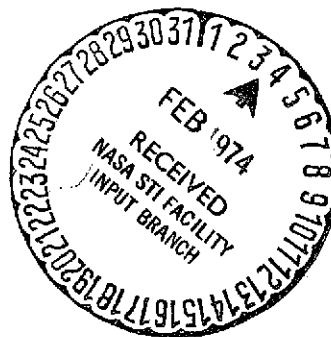
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16. Abstract A discussion of the basic principles underlying bonding in organic phosphorus compounds. A brief review is made of the position of organic chemistry in the chemical field and the primary uses of the compounds with which it deals. Subsequently each of the possible bonding valences for phosphorus are treated in turn: the 3, 4 and 5 coordinations as well as the moreunusual 1, 2 and 6 coordinations. Compounds which are only formally predictable are distinguished from those which have actually been prepared.					
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ON THE STRUCTURE OF PHOSPHORUS COMPOUNDS

R. Wolf

Phosphorus possesses fifteen electrons, only five of which are chemically active. This number, however, is sufficient to enable it to become the cornerstone for a great many structures -- some of them useless, and some of them much too useful.

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The living things and inanimate objects of the tangible world may seem to be subject to infinite variety; in fact, however, centuries of experimentation and analysis have led to the recognition that they have basic structural elements in common: atoms. By chemical analysis of any type of substance it is possible to detect no more than approximately one hundred well-defined chemical elements. The world's infinite variety, therefore, arises from the infinite possibilities for combining these elements.

Chemistry is that science which combines elements with each other in order to form molecular or ionic structures (synthesis), which analyzes reactional mechanisms, and which determines the spatial structure (stereochemistry) and properties of compounds.

Organic chemistry, in its original sense, was directed specifically toward study of the molecules comprising living things at a time when these were believed to differ from molecules prepared in the laboratory. However, since this was found to be an artificial limitation, this science today deals with all effectively realizable molecular structures, basically using carbon (C),

* Numbers in the margin indicate pagination in the foreign text.

hydrogen (H), oxygen (O) and nitrogen (N) atoms.

The organic chemistry of phosphorus only adds a further element to the above partners.

Its methods differ little from those of traditional organic chemistry, and like the latter it has benefited from tremendous advances in synthesis and separation methods, in molecular structure determination, and in theoretical concepts leading to a better understanding of chemical reactivity.

Today separation of products is accomplished by techniques (vapor phase or thin film chromatography) which make it possible to perform studies using very small amounts of matter.

Using spectroscopic methods, which are based on the interaction of electromagnetic radiation (light) with matter, it is literally possible to "read" which atoms are bonded to each other and how this structure, in turn, is linked to the molecular skeleton. With the aid of infrared spectrography, only a few minutes are required to determine whether a compound contains a phosphorus-hydrogen bond, and this result can be confirmed within an hour by means of the nuclear magnetic resonance method. Formerly the same information was obtained by correlating a series of chemical reactions, and weeks or months would elapse before definite results were obtained.

The chemistry of phosphorus has benefited considerably from advances in knowledge on the complex nature of chemical bonding. The research being performed in this area, which is of tremendous importance, follows three basic lines of inquiry: /5

-- fundamental knowledge of the chemical properties of phosphorus,

-- development of directly usable organophosphorus compounds (insecticides, nonflammable materials, drugs, etc.),

-- study of phosphorus derivatives of biological interest.

Three Paths of Research

To judge by the number of publications which appear, there are throughout the world about 3,000 researchers daily amassing new information on this type of chemistry. Among the concerns of this scientific community are: the relative probability of the existence of a molecule, the spatial distribution of charge densities, and the energy and exchange mechanisms of these bonds. This necessary aspect of basic knowledge on the properties of these molecules is perhaps less a primary concern among researchers seeking direct applications.

Thus, organic phosphorus compounds play a large part in combating parasites, from microorganisms to rodents. Here the objective is to discover organophosphorus derivatives with certain well-defined properties. The vulnerability exhibited by insects toward these products, however, also occurs in man, and the chemical warfare arsenal is well stocked with organophosphorus compounds which have been termed "insecticides for humans."

Here a fundamental difficulty arises. We know that knowledge gives power; but the latter is open to use in any direction. The field of research discussed here illustrates this ambiguity.

Although this field is subject to direct use, however, its discoveries often remain confidential, protected by industrial or military secrecy. To give an idea of the vast area covered by this secrecy, it need only be noted that on the average 5,000 pro-

ducts must be synthesized and tested to obtain a commercial insecticide and that there are about a hundred derivatives actually in use.

In another connection, some idea of the importance of the other path of research can be obtained if phosphorus is seen as one of the five elements on which the very origins of life depend. Biochemists attempting to determine the conditions under which the biological processes might have initially begun use as their point of departure a system containing at least five molecules: hydrogen (H_2), water (H_2O), ammonia (NH_3), methane (CH_4) and phosphoric acid (H_3PO_4).

In effect, when a human being moves, for example, blushes, or struggles internally against microbial infection, organic phosphorus derivatives operate at all levels in the cellular machinery. Thus at the end of the day a human being has eliminated 1.5 grams of phosphorus which must be replenished by food: a slice of liver will supply a great deal of phosphorus, and an apple, very little. These derivatives serve an irreplaceable function in all living organisms.

Numerous abbreviations are used in biochemistry which fail to reveal the presence of phosphoric or pyrophosphoric ester functions in some part of the designated molecule. Sometimes the presence of these functions is explicit in the designation used, as for example in adenosine triphosphate (ATP), which participates in the synthesis of all organic compounds and in muscular contraction, or again, in cyclic adenosine monophosphate (cyclic AMP), which is active in all regulatory phenomena. But phosphoric esters are also the basic or discrete constituents of many other indispensable biological structures without actually appearing in their designations. They form an important part of ADN, for example, while on the other hand there is only one atom of phos-

phorus in the 180 comprising vitamin B12.

Although work on these compounds continues, it may be noted that laboratories specializing in research on phosphoric esters of biological interest have relatively little contact with chemists specializing in phosphorus who are dealing with the synthesis of new molecules to determine their structure and properties.

The question remains, what types of information have been obtained in more than a century of activity in the field of organophosphorus compounds? First, it may be estimated that several hundred thousand different molecules have been synthesized and studied in various aspects, and the mass of experiments performed, with the addition of some brilliant insights, have permitted a coherent classification of tremendous amounts of experimental data. A virtual mathematics of electrons exists which is both rigorous and consistent. Thus almost all the molecules which have been synthesized, following strict structural laws, could be predicted before their discovery. In fact, in certain areas of chemistry mathematicians have already determined all the molecules which can be created from a given number of carbon and hydrogen atoms. Their synthesis may be attempted if desired; this may be an extremely long and difficult process, but drawings of the complicated molecule which will be created will have already been published.

To conclude this introduction it may be stated that chemical structure can be understood and appreciated only with an accompanying knowledge -- even if it is cursory -- of the structural laws which we will now attempt to set forth.

Structural Principles

In a given molecular structure phosphorus may be surrounded by one to six atoms as direct neighbors. Because of this fact it is possible to supply a convenient and relatively non-artificial classification. In fact, using an nmr system adjusted for sensitivity to phosphorus it is possible to count the number of neighboring atoms surrounding this atom solely by reading the location of an absorption peak. It should be mentioned that the known compounds are very unequally distributed among these six categories (Fig. 1). Currently configurations of three, four and five atoms are clearly predominant (these are termed 3, 4 and 5 coordinations), and it is therefore appropriate to discuss them first. It should be emphasized that only 25 years ago, the 1, 2, 5 and 6 coordinations were unknown in the organic chemistry of phosphorus.

The events which occur in the molecule when various products are mixed will therefore be described.

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Phosphorus is one of the elements bearing an atomic number of 15, meaning that it possesses 15 electrons (negative charges which gravitate around a nucleus complementarily charged with positive electricity). Strangely, these electrons are subject to a closure principle which makes two of them, and then eight of them, chemically inert. Thus there are only five electrons remaining which play a role in the formation of bonds between atoms. These electrons are distributed in atomic orbitals which are preferential paths defined by energetic aspects and also, to a lesser degree, by geometric aspects. The five electrons follow two types of orbitals and can be subdivided into a 3 + 2 electron system. Other atoms such as nitrogen (N) and arsenic (As) have the same peripheral structure containing five electrons, termed valence electrons, and there are striking similarities among these elements.

These structural analogies are of considerable interest in research toward new organophosphorus compounds.

What happens if one attempts to create the simplest conceivable phosphorus molecule, that is, the molecule resulting from a bond between a hydrogen and a phosphorus atom? The hydrogen atom possesses only a single electron which follows a well-defined atomic orbital.

Schematically, when the hydrogen atom approaches the phosphorous atom, the path of the hydrogen atom -- which we will designate by H^{\bullet} -- converges with that of a phosphorus electron to form what is termed a molecular orbital, and the presence of an electron pair on this new path will result in a bonding force between the two atoms. In this instance, the structure $H : \ddot{P} \cdot$, commonly written $H-P$, is formed (the hyphen denoting the pair of bonded electrons). This structure does exist, but only under very exceptional conditions (high temperatures, electrical discharge in an appropriately gaseous mixture, etc.). It can be seen that in order to obtain a stable molecule, the three external phosphorus electrons with the same energy must be used simultaneously, and as a result, the simplest accessible molecule is H_3P ; hydrogen phosphide, in which a doublet of phosphorus electrons is not used. This compound is a toxic gas with a highly unpleasant odor.

This first structural principle, the placing of two electrons in parity, may already serve as a basis on which to predict a large number of possible molecules. In fact, any atom or group of atoms with an available peripheral electron may make three bonds with a phosphorus atom, resulting in a compound of the general type X_3P .

1. Nombre très approximatif
de dérivés connus (1972)

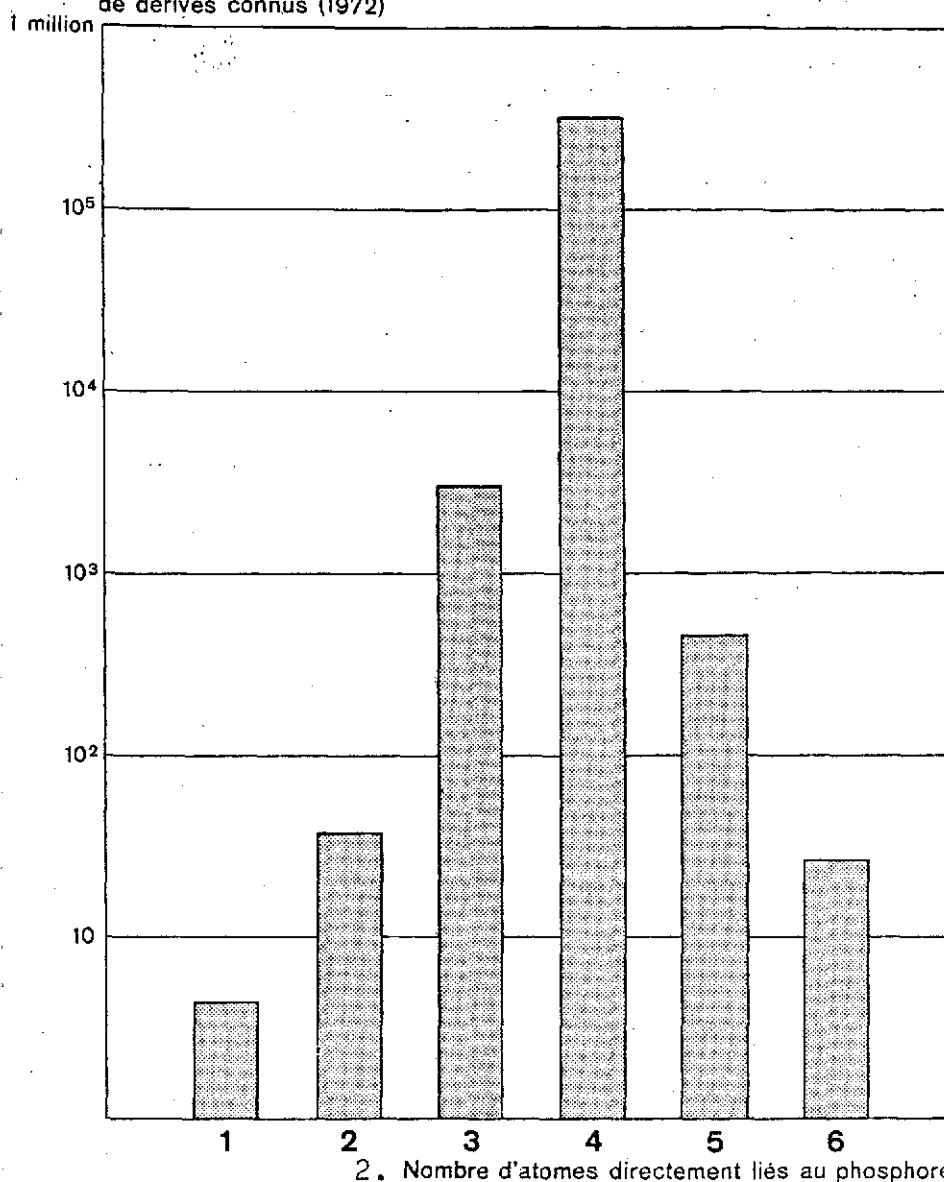
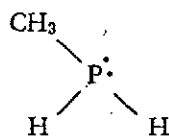


Fig. 1. In one molecule, a phosphorus atom may be directly bonded to one, two, etc., up to six atoms. The diagram shows the current number of known phosphorus compounds in which the atoms possess one, two...or six direct neighbors. Currently the most numerous organophosphorus compounds known are those whose phosphorus atoms have three, four and five direct neighbors.

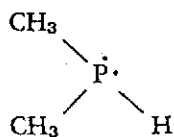
Key: 1. Number of known derivatives, highly approximate (1972).
2. Number of atoms directly bonded to phosphorus.

If the bond phosphorus is able to make with methane (CH_4) is considered, for example, it can be seen that the structure $\text{CH}_3\cdot$ is capable of performing the same function as hydrogen, and one can therefore construct:

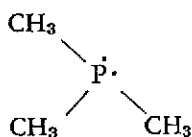


then

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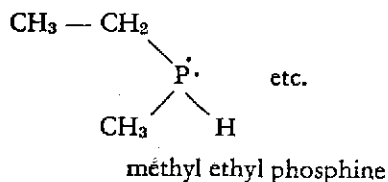


and



These three derivatives, which are termed methyl phosphines, were among the very first organic phosphorus compounds to be synthesized.

With these three derivatives one may subsequently use any one of a thousand configurations to remove a hydrogen atom H from the $-\text{CH}_3$ group to replace it with another $\text{CH}_3\cdot$, making it possible to obtain:



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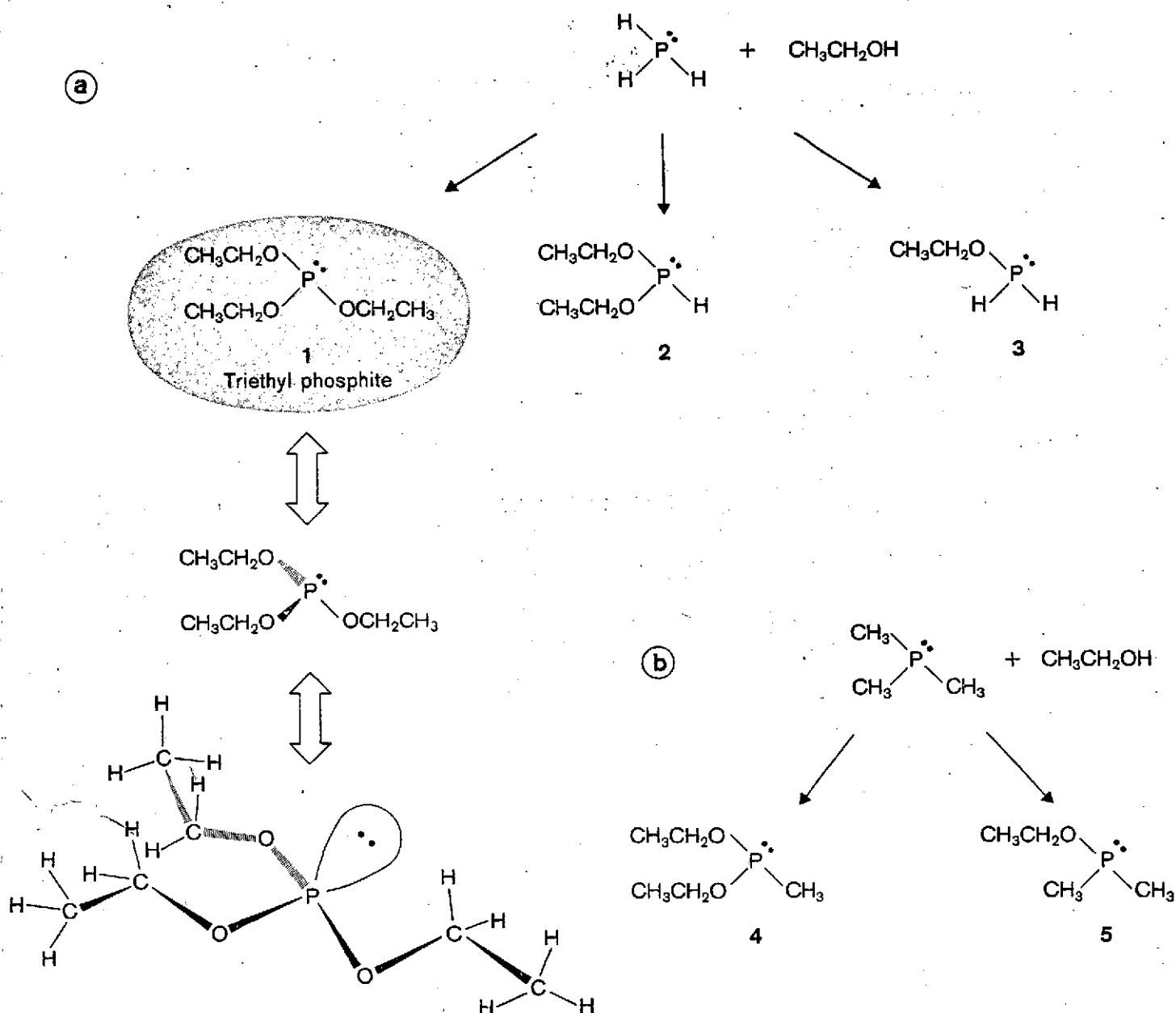


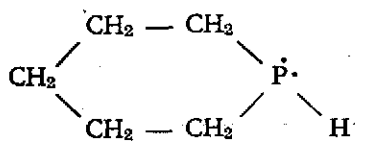
Fig. 2. Numerous derivatives of phosphine PH_3 (a), trimethyl phosphine (b) and ethyl alcohol $\text{CH}_3\text{CH}_2\text{OH}$ can be formally conceived. The radicals $-\text{H}$, $-\text{CH}_3$, and $-\text{OCH}_2\text{CH}_3$ are in fact chemically replaceable.

Triethyl phosphite (1) is an important derivative since it is used as a point of departure for a large number of syntheses. (2) has

existed only since 1970, while (3) is yet to be discovered. Derivative (4) has been named phosphonite, and (5), phosphinite; the difficulties involved in naming the products discovered, as well as in writing their formulas, are obvious.

The chemist must continually use increasingly concise formulas to designate a single molecule; here triethyl phosphite is written in three equivalent ways.

Still more complex operations may be performed by theorizing that two atoms of a single molecule are able to bond to each other actually within the structure. Phosphorinane, for example, is obtained by formation of a six-atom cycle:



By formally producing a reaction between any of these derivatives and ordinary alcohol, with the formula $\text{CH}_3\text{-CH}_2\text{-OH}$, a large variety of compounds can further be constructed. (Fig. 2).

Thus there is little difficulty in imagining the tremendous number of molecules which may be formed by the thousands of radicals offered by organic chemistry. If there are 10,000 derivatives in this series of tricovalent phosphorus compounds (which will be designated by P^{III}), these are only the beginning of a vast number of possibilities. In practice, however, difficulties will frequently be encountered in dealing with the simplest derivatives, even if their preparation should be possible according to the mathematical aspects of the electrons.

Two points should be emphasized in regard to those compounds where phosphorus has three neighboring atoms:

* The process of removal of a hydrogen atom and its replacement by a radical is a convenient means of describing possible operations, but in actuality it is seldom possible to prepare

these compounds by means of this process; the chemist's job is therefore to find the best route among the large number of known reactions.

* The geometry of molecules containing a tricovalent phosphorus compound is known in many cases; the three bonds cannot be and are never distributed within a plane (that is, they are not coplanar). Their directions are intermediate between those of the three edges radiating from the corner of a cube and the lines emanating from the center of a regular tetrahedron. Several possible explanations have been offered for this geometry (Fig. 3).

* When two phosphorus derivatives are spontaneously mixed at ordinary temperatures, the substituents of the phosphorus will pass from one molecule to the other, and this exchange of radicals is governed by principles involving the respective stabilities of the derivatives, their statistical distributions, and an energy barrier which must be crossed for the reaction to take place.

Introduction of a Fourth Neighboring Atom

All tricovalent phosphorus compounds possess as a common characteristic a doublet of free electrons, or in other words, a reaction potential which can be brought into play by two mechanisms:

(a) by bond formation between atoms which share four electrons, each of them supplying two (Fig. 4),

(b) by bond formation using two electrons in which phosphorus P^{III} supplies the sole necessary electron pair.

On this basis one can envision the possibility of successively introducing a fourth neighbor -- carbon, nitrogen, oxy-

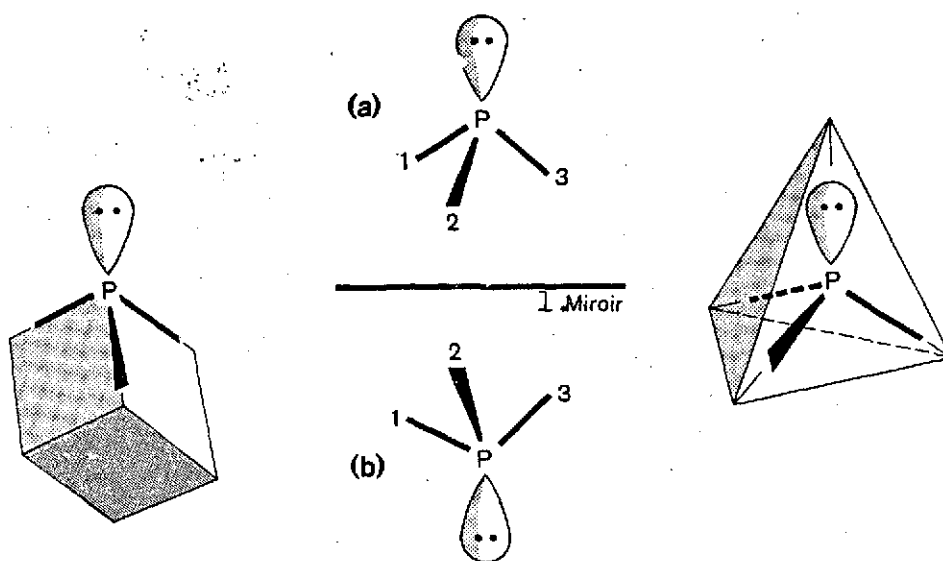
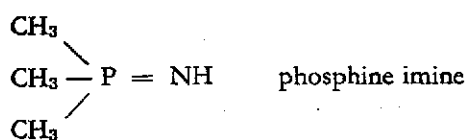


Fig. 3. Approximate orientations of the bonds around a phosphorus atom with three neighboring atoms. The orientations are intermediate between those of the three edges radiating from the corner of a cube and the lines emanating from the center of a regular tetrahedron. One possible explanation for this geometry is that the atomic orbital electron paths of the phosphorus converge to result in the geometry observed (hybridization); another is that the bonds and the electron pair repulse each other to produce the observed shape. When the three neighboring atoms around P are different, the mirror image of (a), that is, (b), cannot be superimposed on (a). The two compounds do exist; they are isolable, and they are currently the subject of active research. The same phenomenon will be observed for phosphorus compounds with four, five or six neighboring atoms, where the molecule-object/molecule-image pair will not be superimposable.

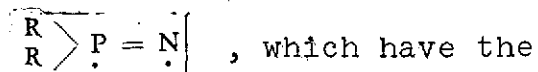
Key: 1. Mirror.

gen, etc. -- into phosphorus P^{III} .

Introduction of an nitrogen radical, for example, makes it possible to obtain the molecule:



from which one can derive compounds with the general formula



, which have the general property of bonding among themselves to form cycles. Thousands of cycles of this type exist.

If cycles of all sizes exist, linear chains are also possible given that $\left[\begin{array}{c} \text{R} \\ \text{R} \end{array} \right] \text{P} = \text{N} \cdot$

with n being as high as 15,000. When the radical R is properly selected, the polymers obtained possess unusual properties such as the ability to remain flexible and elastic at temperatures as low as -80°C . Thus the insulating encasing of electrical wires in a device in use at the South Pole gives some indication of the chemistry of phosphorus.

In practice, the fourth bond around a P^{III} phosphorus atom is most often made using the available doublet of certain atoms such as oxygen (O), sulfur (S) or selenium (Se) (Fig. 5).

Biologically active molecules are basically phosphoric esters with the approximate composition: $(\text{CH}_3\text{CH}_2\text{O})_3\text{P} = \text{O}$; it is perhaps not surprising to learn that there are structural similarities between these biological phosphoric esters and the tremendously active products used in chemical warfare.

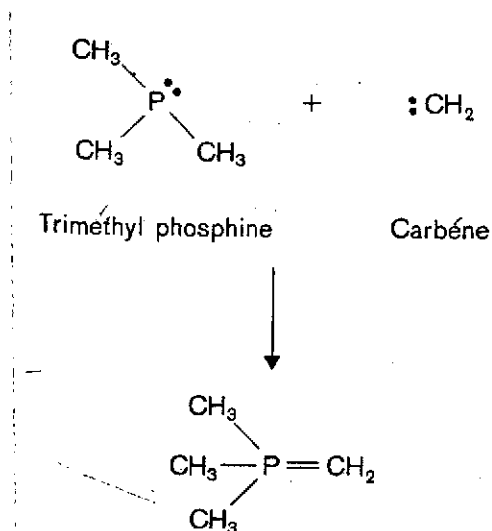


Fig. 4. Stable chemical structures such as trimethyl phosphine or unstable structures such as carbene, each with an electron doublet available, would be capable of combining to produce a known molecule. This molecule would simultaneously possess phosphorus-carbon bonds containing two ($\text{P}=\text{CH}_2$) or four electrons ($\text{P}^+::\text{CH}_2^-$).

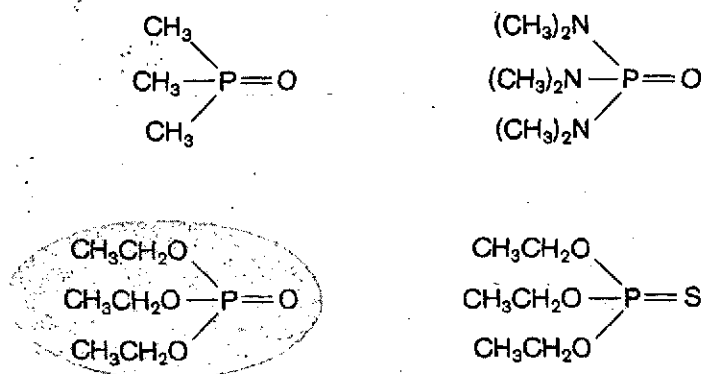


Fig. 5. These four molecules in which phosphorus is surrounded by four atoms which are directly bonded to it are representative of tens of thousands of analogous molecules. Triethyl phosphate, shaded in gray, is comparable to biologically active phosphoric esters.

A very large number of pesticides with unusual names belong to this family of phosphorus compounds: nemaphos, nogos, parathion, methepa, thiothepa, diazinon, and a hundred others. Their effects range from paralysis to sterilization of insects. The toxicity of these derivatives to man is far from negligible, and, on the other hand, a large number of these pesticides are the systemic type (that is, they penetrate into the sap of plants). Frequently the operation of testing for the possible presence of these products in food is performed at the expense of the daphne; the mortality of a colony of these water fleas makes it possible to detect, for example, 0.1 mg of toxic product in a kilogram of grapes.

Unusual Coordinations

Passage from tricoordinated derivatives (P^{III}) to penta-coordinated derivatives (P^{V}) can now be considered without introducing new concepts.

All phosphorus molecules with five neighboring atoms result, at least formally, from the combination of two molecules, each of which is often stable in itself. The existence of such pairs has led to the promising concept of hypermolecules. Ever since the first P^V organophosphorus structure was known, the geometry of such molecules has been problematic. This is now known to be a trigonal bipyramid (Fig. 7). In this model, the bonds using three of the five neighboring atoms form angles of 120° , with these atoms determining an equatorial plane; the fourth and fifth atoms are located above and below this plane in the "apical" or "axial" positions.

Let us now shift our consideration from compounds in which phosphorus is surrounded by three, four or five neighboring atoms to the field of 1, 2 and 6 coordinations, which are much more unusual at the present time.

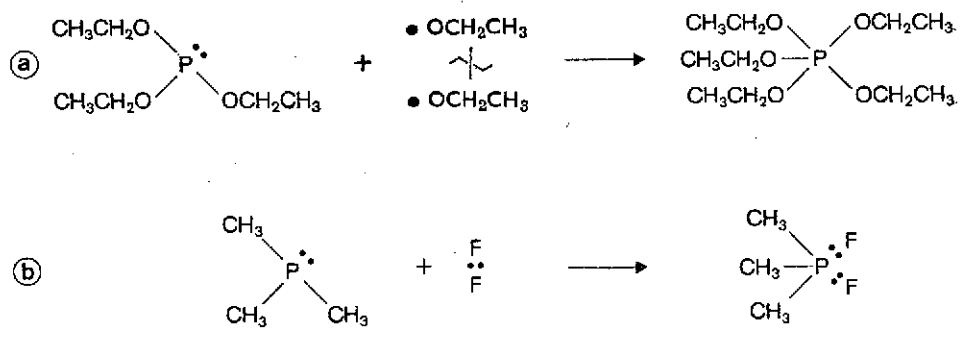


Fig. 6. Two fragments of molecules, each carrying an electron, may separate the free doublet of a P^{III} , and the result, after the formation of two bonds each containing an electron pair, is a compound in which phosphorus has five neighboring atoms. Triethyl phosphite is capable of reacting with two ethoxy groups, OC_2H_5 . (a) This excellent experiment, which uses ethyl peroxide $EtO\cdot OEt$, cut by the effect of light following a dotted pattern, was puzzling to a great many chemists who expected a different outcome. (b) Theoretically any molecule, divided into two parts at a simple bond with the two electrons shared, may be added to a tricovalent phosphorus derivative.

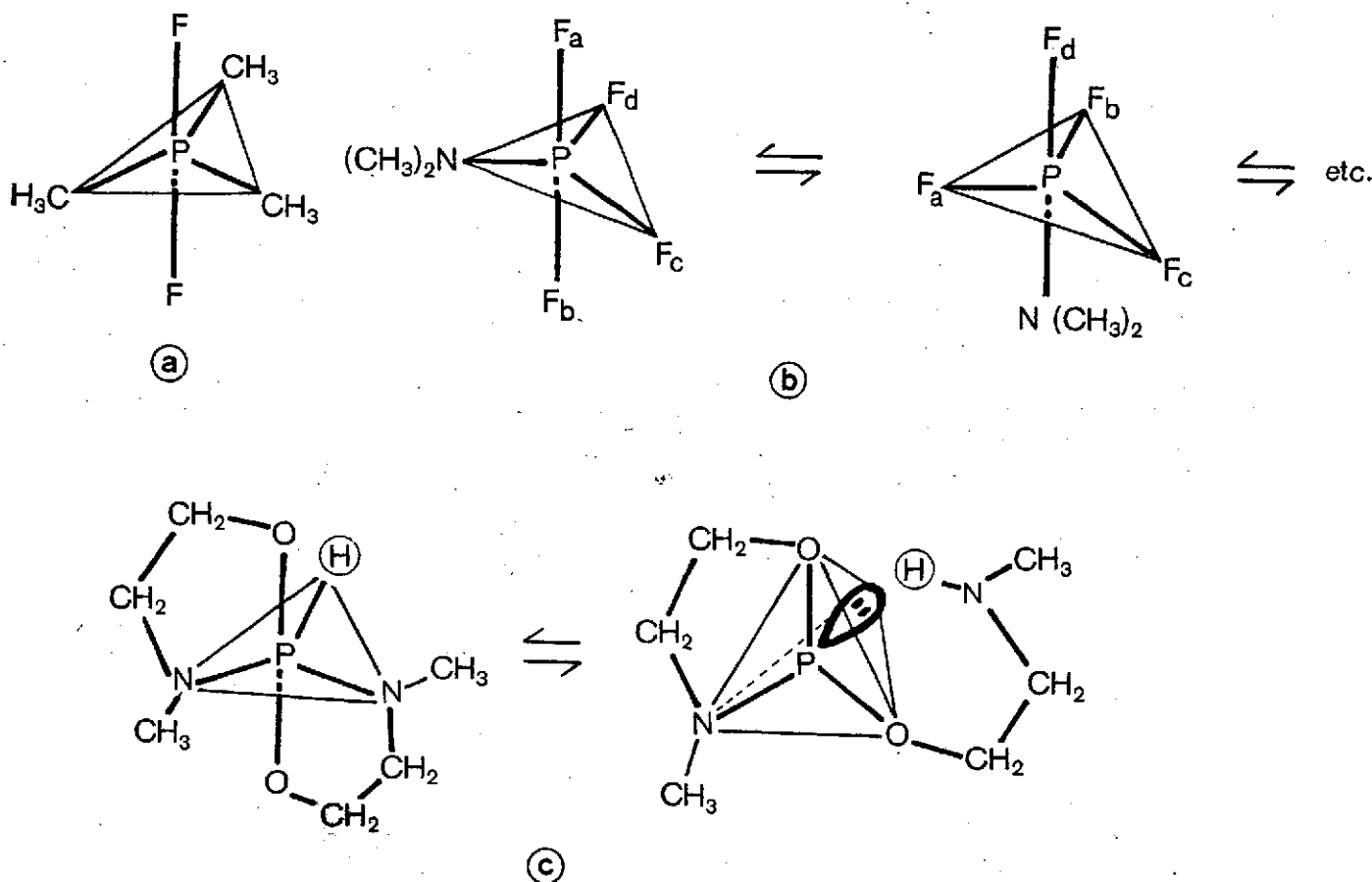


Fig. 7. (a) The geometry of the $(\text{CH}_3)_2\text{F}_2\text{P}$ molecule is that of a trigonal bipyramid. The atoms which are directly bonded to phosphorus are not randomly located in the structure; here, the fluorine (F) atoms preferentially occupy the axial positions.

(b) When the molecule receives an excitation energy the substituents may trade positions and enter a different distribution on the same trigonal bipyramid without breaking their bonds with P.

(c) These molecules are in equilibrium with each other; the circled hydrogen H has no bonding preference between phosphorus and nitrogen. Phosphorus here vacillates between five neighboring atoms (trigonal bipyramidal geometry) and three neighboring atoms (tetrahedral geometry). This is the phenomenon of tautomerism.

The chemistry of nitrogen has permitted the discovery of a new possibility for phosphorus bonding. A well-known (and extremely dangerous) derivative of nitrogen is hydrocyanic acid, $\text{H}-\text{C}\equiv\text{N}$. Thorough knowledge of the mathematics of electrons has suggested that nitrogen might be replaced by a phosphorus atom, and the analogous phosphide of hydrocyanic acid does actually exist. It is not easily accessible, however, and the synthesis of $\text{HC}\equiv\text{P}$ can be carried out only under exceptional conditions. The existence of this derivative indicates that phosphorus may well use three electrons to form a single bond; this situation, which frequently occurs with nitrogen, is exceptional for phosphorus. The nitrogen molecule $\text{N}=\text{N}$ is stable (this is the state in which nitrogen occurs in the air); on the other hand, if $\text{P}=\text{P}$ exists it does so only toward 800°C . So far very little is known about such compounds, in which phosphorus uses three electrons to form a single bond, but the fact that such bonding is at all possible offers considerable promise.

Elements are currently known which make it possible to theorize the existence of molecules in which phosphorus is surrounded by two atoms. The priority principle, according to which three phosphorus electrons may be used independently, immediately offers a satisfactory pattern of 2 electrons + 1 electron to form two bonds, one with two electron pairs and the other with a single pair. Here again a very large number of nitrogen derivatives are known in which nitrogen is surrounded by two atoms sharing three electron pairs. The possible analogy with phosphorus and arsenic makes it possible to conceive of compounds of the same type for these two elements; the first derivatives were produced about ten years ago (Fig. 8). It now remains to consider the formation of six bonds by a phosphorus atom.

When a phosphorus atom has used its five electrons to form

bonds one may assume that it is therefore no longer reactive. In reality, however, the phosphorus atom will tolerate greater external electron packing. In fact, not only will it easily form derivatives in which it is surrounded by five electron pairs, but it will also form a sixth bond with a partner capable of providing it with a pair of available electrons (Fig. 9).

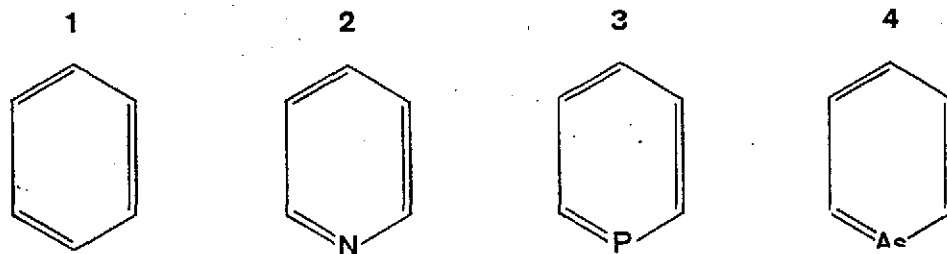


Fig. 8. For some time a molecule similar to benzene (1) has been known in which a $-\text{CH}=$ group is replaced by a nitrogen atom; this is pyridine (2). The possible analogy with phosphorus and arsenic has made it possible to predict compounds 3 and 4, whose preparation has been extremely problematic; this was not accomplished until 1971.

The series of molecules shown in the figure is extremely interesting from a theoretical standpoint. Theoretical chemists, who have greatly increased our understanding of the nature of chemical bonding, are beginning to undertake complex quantum mechanical calculations using computers. This effort is unusual in the sense that it is an attempt to produce a unitary mathematical representation of a given molecule from which it will be possible to determine all its observable properties a priori.

At a time when biology and data processing are considered to be of more current interest, chemistry, although less publicized, nevertheless remains an active and inexhaustible source of knowledge. The structures it forms follow rules as strict as those of a game of chess.

One should not fail to recognize, however, that achievements in the chemistry of organophosphorus compounds have been /11

questionable from a moral standpoint. This problem, which harks back to the production of metal for agricultural tools and is undeniably a difficult one; but it is my belief, after K. Lorentz, that mankind may reach a stage of evolution at which aggression, although formerly useful, will dissipate for lack of purpose.

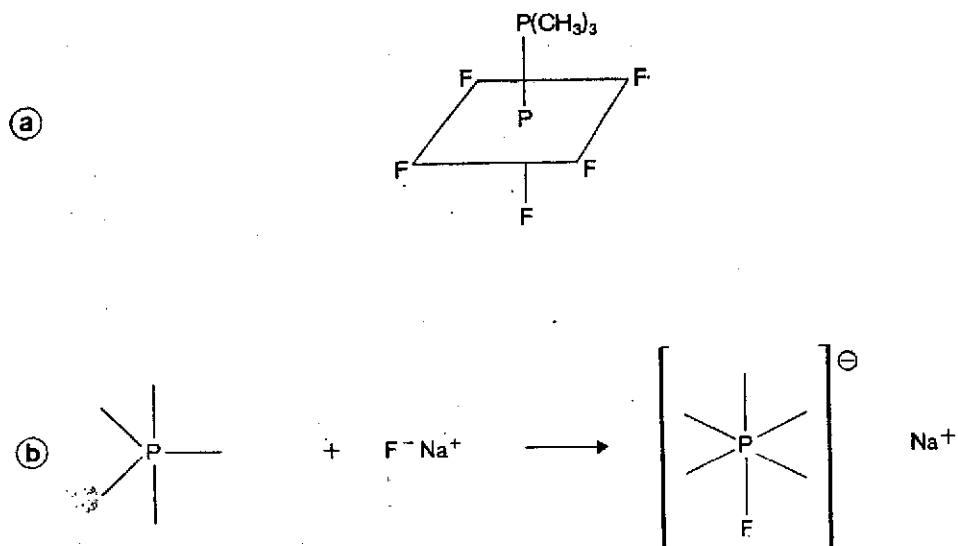


Fig. 9. The phosphorus atom is capable of forming up to six bonds within a molecule.

For example, trimethyl phosphine $(\text{CH}_3)_3\text{P}$ gives a well-defined compound with phosphor pentafluoride PF_5 .³ In this molecule (Fig. 9a), one phosphorus atom is surrounded by four atoms and the second by six; the geometry of the atoms surrounding the latter is octahedral.

Electrically charged bodies such as anions may carry the electron doublet necessary for the formation of a sixth bond with phosphorus (Fig. 9b).

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